

REMOVAL OF GLASS ADHERED TO SINTERED CERAMICS IN HOT
ISOSTATIC PRESSING

No Author Given



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14. Abstract In the hot isostatic pressing of ceramic materials in molten glass using an inert gas as a pressing medium, glass adhered to the sintered ceramics is heated to convert it to a porous glass and removed. Thus, Si_3N_4 powder was compacted at 5000 kg/cm^2 , coated with 0.5 mm-thick BN, embedded in Pyrex glass in a graphite crucible, put inside a hot isostatic press app. contg. Ar, hot-pressed at 1750° and 1000 kg/cm^2 , cooled, taken out, from the crucible, heated at 1100° for 30 min, cooled, and then glass adhered to the sintered body was removed. <div style="text-align: right;">ORIGINAL PAGE IS OF POOR QUALITY</div>			
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Specification

1. Name of the Invention: Removal of glass adhered to sintered ceramics in hot isostatic pressing /401*

2. Claim

1. In the method of removal of glass adhered to sintered ceramics in hot isostatic pressing the compact which is to be processed is enclosed in glass container under high temperature and the abovementioned compact is sintered under pressure where an inert gas is set as the pressing medium. And borosilicate glass was used for the above mentioned glass material. After the sintered body of the compact was completed by the process of hot isostatic pressing, the pressure medium which was fused in glass is evaporated and the glass is made porous. After that the glass was cooled off in this porous condition and the porous glass adhered to the surface of the sintered body was removed.

2. The method of removal of glass adhered to sintered ceramics in hot isostatic pressing stated in item No. 1 of the claim, in which borosilicate glass is Pyrex (registered trade mark) which includes SiO_2 80.6%, B_2O_3 8.32%, Al_2O_3 2.0% and (illegible).

3. This is a method of removal of glass adhered to sintered ceramics in hot isostatic pressing stated in item No. 1 or item No. 2 of the claim in which, after sintering by the process of hot isostatic pressing, the compact which is covered with glass is taken out by cooling in the same pressing process equipment. And after that the compact is heated again and the glass is made porous.

4. This is a method of removal of glass adhered to sintered ceramics in hot isostatic pressing stated in item No. 1 or No. 2 of the claim in which the glass is made porous by lowering the pressure at a constant high temperature in the pressing process equipment after sintering by a hot isostatic pressing process.

5. This is a method of removal of glass adhered to sintered ceramics in hot isostatic pressing stated either in item No. 1 or No. 4 of the claim in which the pressing medium gas is Ar gas.

6. This is a method of removal of glass adhered to sintered ceramics in hot isostatic pressing stated in either item No. 1 or No. 4 of the claim in which the pressing medium is N_2 gas.

7. This is a method of removal of glass adhered to sintered ceramics in hot isostatic

* Numbers in margin indicate foreign pagination

pressing stated either in No. 1 or No. 6 of the claim in which the powder which is processed is a ceramic powder.

8. This is a method of removal of glass adhered

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to sintered ceramics in hot isostatic pressing stated in item No. 7 of the claim in which the ceramic powder which is processed is chosen from either silicon nitride, silicon carbide or boron carbide.

9. This is a method of removal of glass adhered to sintered ceramics in hot isostatic pressing stated in either item No. 1 or No. 6 of the claim in which the powder which is processed is a metallic powder.

10. This is a method of removal of glass adhered to sintered ceramics in hot isostatic pressing stated in either item No. 1 or No. 9 of the claim in which the compact which is processed, as well as the mold release agent, is placed at the interface of the glass.

3. Explanation of the invention in detail

This invention is about an effective removal procedure of glass adhered to sintered ceramics in order to remove the glass adhered to products after processing by the abovementioned hot isostatic pressing method, especially when glass is used as the sealant.

There are some advantages to the procedure of hot isostatic pressing (abbreviated as HIP from now on) in which glass is used as the sealant, such as profile molding is possible and also even under high temperature in which copper, steel, etc. cannot normally be used for capsule material, HIP is sufficiently possible. Especially, the practical use of HIP has been strongly advanced as a molding and processing method for ceramics. This is an expected development as there are comparatively plenty of raw materials for ceramics, ceramics are sufficiently strong at high temperatures, and they also have a high heat capacity. And the glass capsule method (refer to patent No. 1971-2731 official report, etc.), and method of processing a compact which is put in glass grains (refer to patent No. 1980-89405 official report, etc) are publicly known. However, there are some problems in this HIP procedure, such as that glass attaches to products and since the glass attaches strongly, it is often hard to remove it. Presently, external mechanical forces, such as hitting glass with a hammer, are used but, since extremely strong forces are

required, there are some disadvantages such as removing glass attached to uneven parts of the molding surface. Especially, when glass capsules are used, while temperature is dropping after HIP, the glass breaks and separates because of the differences in coefficients of thermal expansion between compact and glass. Because of that, there is an opinion that removal of glass is extremely easy; but in fact removal of glass is not only very difficult but also, depending on the differences in the coefficients of thermal expansion, the main body and corner part often break since glass is pushed into the compact bore by the pressing force; and also, glass and Si_3N_4 , which is the powder to be processed, react.

Needless to say, in the case of silica glass, removal of glass becomes easier by controlling the cooling rate and making the glass crystallize. But, in the case when reaction of glass with compact also occurs, silica glass does not often crystallize about 0.1 - 0.2 mm from the compact surfaces, and removal of glass is difficult. In response to the abovementioned circumstances, material in which pressing medium gas penetrates into the glass sealant is chosen to eliminate these deficiencies and a method for easily removing glass attached to products after the HIP procedure is supplied. For the abovementioned glass material, borosilicate is used and after the compact is sintered by the HIP procedure, pressing medium which was fused into glass is evaporated and the glass is made to be in a porous condition. And after that, the glass is cooled off in the porous condition and the porous glass attaches to the sintered body surface.

Here, the abovementioned borosilicate glass is so-called Pyrex glass and its representative composition includes SiO_2 80.6%, B_2O_3 8.32%, Al_2O_3 2.0%, Na_2O 3.8%.

The basic characteristics of this invention are as follows. Ar or N_2 gas, which is used for the pressing medium of the HIP process, is fused in this glass. So, it is easy to make the glass porous after this procedure and these materials in which this pressing medium is dissolved are used for glass sealant.

In the case of silica glass, it cannot be used for this invention for the above reasons. Also, in the case of Pyrex glass it is recognized the same as this invention that if Ar gas is

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made as the pressing medium in HIP, Ar gas is dissolved in glass as pressing medium and, after HIP processing, if the compact which is covered with glass is heated at atmospheric pressure, pressing medium gas evaporates and it is recognized that the glass has a tendency to foam. But, it is considered that in order to make glass foam, it is necessary to heat it to over 1600°C , and it is not very productive. But it is sufficiently possible to use this method in the case when a temperature of

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over 1600°C does not affect the compact. Therefore, this invention begins from HIP processing of powders which are processed by using Pyrex glass. The powder which is processed in this invention is metallic powder or ceramic powder and in the case when either silicon nitride (Si_3N_4), silicon carbide (SiC), and boron carbide (B_4C) is the main component, it is suitable for heat resistant materials and it is very useful.

And this invention is to perform HIP processing by sealing, with Pyrex glass, a preformed body in which these powders or the above mentioned powders, including sintering assistant are present, or presintered body in which the preformed body is sealed with Pyrex glass. There are two kinds of methods for coating the material with glass. One is to enclose the above compact in a so-called glass capsule for HIP which is formed as a container shape and the other is to coat by heating the above-mentioned compact above its softening point by putting in the glass granules. It is possible to use either method, but in the former case in order to avoid the influence of residual gases at the time of enclosure, degassing and sealing are performed. At that time, since the degassed area is only in the capsule, degassing is rather simple. On the contrary, in the latter case it is a little different from the former case as it is necessary to degas the inside of the entire heating furnace. But, in either case it is favorable to arrange the mold release agent interface between the compact and the glass to avoid reaction of glass toward bore in the compact. For example, in the case of Si_3N_4 , either the abovementioned precompact or a presintered body is put in BN powder and they are molded under pressure. In that case it is favorable to make the width of the BN mold release agent over 0.3 mm.

As mentioned above, HIP process is performed through a mold release agent and also by heating the entire surface which is coated with Pyrex glass, in a high temperature and

high pressure furnace for HIP.

And, there is also a case of heating the compact in a crucible for an HIP furnace, so that it will not be broken or contaminated by the flow of glass at the time of HIP process.

Atmospheric gas, such as Ar, or N_2 , etc. gas is usually introduced into HIP furnace as primary pressing medium and an isotropic compression process is performed by making the temperature and pressure of the gas high. But, the relationship between raising temperature and raising pressure is extremely subtle. If the rate of raising pressure is too fast, then for glass capsules, there is a case that strain occurs locally in the glass and the capsule breaks. Also, in the case when glass granules are used, HIP processing can become impossible as high pressure gas infiltrates into the glass granules before a minute glass layer is formed on the above mentioned block surface as glass granules are fused mutually. Therefore, first of all, temperature is raised above the softening point of glass at a pressure of below 100 atmospheres to make plastic flow of the glass possible. Also, in the case when glass granules are used, each granule fuses with others and a minute glass layer is formed on the external surface of the block. And then temperature and pressure are raised to specified HIP temperature and pressure.

HIP temperature is over 1500°C , favorably $1600 \sim 1900^{\circ}\text{C}$, but HIP temperature has to be necessarily under the temperature of decomposition of powders like Si_3N_4 , etc. This temperature becomes high accompanied with a rise of HIP pressure, but it is favorable to perform the HIP processing at least 100°C lower than the decomposition temperature at that pressure at the time of HIP processing.

Next, a pressure of over 500 atmospheres is good for HIP pressure, and if it is below 500 atmospheres, it takes a long time for HIP processing and also the amount of decomposition reaction of Si_3N_4 , etc. becomes larger proportional to time. Because of that, weight of the sintered body is decreased, and also it becomes difficult to attain high density. Therefore, HIP pressure is made at least 500 atmospheres, favorably over 700 atmospheres.

On the other hand, as HIP pressure is higher, decomposition reaction of compact which is processed is controlled, and it is easy to attain a high density.

But, time is required for raising pressure, and also the equipment for HIP processing such as a compressor for raising pressure, pressure vessel of this equipment, etc. are large, so it is not practical. Therefore, it is practically desirable to process HIP at 2500 atmospheres. Also, HIP processing is normally performed in the range of 20 minutes to 5 hours.

Namely, BN powder which is the secondary pressing medium is easily removed with a simple method after HIP processing.

As mentioned above, since the Si_3N_4 sintered body on which HIP processing is performed is blocked with BN, no reaction layer toward glass grows on the surface. And, there is no occurrence of defects or cracks at the corners of sintered body based on the differences in coefficients of thermal expansion between the body which is processed and the glass. And, the sintered body becomes a high density sintered body at over 98% relative density.

As above, HIP processing of compact which is processed is performed by using Pyrex glass, but in this case it is recognized that there is a tendency that pressing medium gas such as Ar gas, etc. is fused in Pyrex glass. But, incomplete sealing, which decreases the effect of HIP processing, is not recognized. Therefore, using this tendency, this invention performs removal of glass sealant after HIP processing.

Namely, the surface of the above-mentioned compact for which temperature and pressure were raised by HIP processing is covered with Pyrex glass. But, pressing medium gas is fused in it and this gas is evaporated again later. There are some chances for the gas to evaporate. One is that the gas is removed after cooling it under high pressure in HIP equipment, namely the inside of HIP furnace, and it is heated again under atmospheric pressure. In the case when it is heated again under atmospheric pressure, for example, electric furnace, etc. there is a case that pressure is lowered with high temperature in the furnace after sintering by HIP processing. Of course either case is the same, but the former case is more advantageous from a practical point of view.

In the former case when the gas is reheated, the compact which is covered with glass is heated to about 1000°C ~ 1100°C under atmospheric pressure. Also, in the latter case it is necessary to realize the situation of evaporation by lowering pressure properly, and the

degree of lowering pressure is determined by understanding the situation of evaporation. But, it has to be cooled off once for removing from compact, so it is more disadvantageous than the former case. The evaporated gas makes the glass foam and if it is cooled off as is, it becomes possible to easily remove glass by applying a small mechanical force.

Namely, even if there are some changes in the porous condition of glass depending on the situation of evaporation, foaming gives the glass a brittle characteristic. Therefore, removal of glass can be performed without great effort and removal of materials is quite easy.

Because of that, this invention makes the removal of glass sealing material easy without causing defects or the occurrence of cracks in the sintered body material after HIP processing, which was one of the outstanding problems. It also simplifies the work of HIP processing, and promotion of industrialization of this process is expected.

The following are explanations of further concrete embodiments for this invention.
(Embodiment 1)

Si_3N_4 powder with a mean grain diameter, of about $1\mu\text{m}$ and about 70% "a" phase was compacted by isostatic pressing at 5000 kgf/cm^2 pressure, and a 62% relative density compact was obtained. BN was coated on this compact surface to a depth of 0.5 mm and it was put in a graphite crucible after it was put in Pyrex glass powder, and it was inserted into the HIP equipment. Next, degassing was performed and the inside of the HIP equipment was replaced with Ar gas. After that it was kept at 1200°C with 10kgf/cm^2 pressure, and furthermore the temperature and the pressure were raised to 1750°C and 1000 kgf/cm^2 . After HIP processing, the temperature was dropped to 500°C keeping the pressure at 1000kgf/cm^2 , and next the pressure was decreased and also the temperature was decreased. The compact which was coated with glass was removed from the crucible and it was put in an electric furnace where the temperature was raised to 1100°C . After this, it was kept in the furnace for 30 minutes, and it was cooled off. The glass which was covering the compact became foamed glass and it was extremely easy to remove it. The compact became a high density sintered body of 98.5% relative density.

(Embodiment 2)

Si_3N_4 powder with a mean grain diameter of about $1\mu\text{m}$, and about 70% "a" phase was

compacted by isostatic pressing at 5000kgf/cm² pressure, and a compact of 62% relative density was obtained. 0.5 mm depth BN was coated on this compact surface and it was placed in a graphite crucible and put in Pyrex powder and it was inserted in HIP equipment. Next, after being degassed, the inside of HIP equipment was replaced with Ar gas, it was kept at 1200°C with 10 kgf/cm² pressure and furthermore the temperature and pressure were raised upto 1750°C and 1000 kgf/cm² respectively. After HIP processing the temperature was decreased to 1100°C and the pressure was decreased to 10 kgf/cm² and it was kept for [30] minutes. The glass which was covering the compact became foamed glass and after that the temperature was decreased and the compact was taken out. The removal of the glass was extremely easy.

The compact became a high density sintered body with (illeg.) 5% relative density the same as embodiment 1.

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